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**VIA FEDERAL EXPRESS**

February 1, 1999

Mr. Daniel Rodriguez Corchado
Environmental Engineer
U.S. Environmental Protection Agency
Caribbean Environmental Protection Division
Centro Europa Building, Suite 417
1492 Ponce de Leon Avenue
San Juan, Puerto Rico 00907-4127

Mr. Clifford Ng
U.S.E.P.A., Region II
Air and Waste Management Division
290 Broadway
New York, NY 10007-1866

Re: Proteco's Post-Closure Permit Application

Dear Messrs. Rodriguez and Ng:

Annexed please find a copy of Proteco's proposed Dye Tracer Study Work Plan. As set forth in the Work Plan, Proteco has proposed to undertake a dye tracer study to determine whether groundwater monitoring will be required as part of Proteco's post-closure activities.

The annexed Work Plan constitutes a part of Proteco's post-closure permit application. It is expected that the rest of the application will be submitted under separate cover shortly. However, as we previously discussed, Proteco is submitting the annexed Work Plan now to expedite resolution of the post-closure groundwater monitoring issue.

Proteco requests that EPA expedite its review of the annexed Work Plan. Please do not hesitate to call me if you have any comments or questions.

Sincerely,

Sy Gruza

SG:lb

Enclosure

cc: Amy Chester, Esq.
Dr. Jorge Fernandez
Mr. Steven Young

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# DYE TRACER STUDY WORK PLAN

# FOR

# PROTECO RCRA UNIT CLOSURES

**PEÑUELAS, PUERTO RICO**

**Submitted to:**

## UNITED STATES ENVRONMENTAL PROTECTION AGENCY

## REGION II

**NEW YORK, NEW YORK**

**FEBRUARY 1, 1999**

# DYE TRACER STUDY WORK PLAN
# FOR
# PROTECO RCRA UNIT CLOSURES

## PEÑUELAS, PUERTO RICO

**Submitted to:**

**UNITED STATES ENVRONMENTAL PROTECTION AGENCY**
**REGION II**

**NEW YORK, NEW YORK**

**Prepared for:**

**PROTECO**

**Peñuelas, Puerto Rico**

**Prepared by:**

**Law Environmental – Caribe**
**San Juan, Puerto Rico**

**In association with**

**Law Engineering and Environmental Services, Inc.**
**Kennesaw, Georgia**

**Project 12000-7-0221**

**January 29, 1999**

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## LIST OF APPENDICES

# 1.0 INTRODUCTION

## 1.1 OBJECTIVES

In accordance with discussions between USEPA Region II of the United States Environmental Protection Agency (USEPA Region II) and PROTECO regarding post-closure ground-water monitoring plans, PROTECO agreed to submit a Dye Tracer Study (Study) Work Plan. The objective of this Study is to resolve concerns about the possibility for migration of Constituents of Concern (COCs) into the limestone underlying the Juana-Diaz Formation clayey sediments at PROTECO's Peñuelas Site (Site). The Site includes the 13 RCRA waste management units presently being closed in accordance with the closure plan approved by USEPA Region II. The results of the Study will address USEPA Region II's concerns about the potential for migration of COCs off site toward human and ecological receptors that may be exposed to ground water from the deep limestone deposits.

The results of the Study will be evaluated and used to determine whether post-closure ground-water monitoring is required for the closed RCRA units. If the Study demonstrates that there is a potential for downgradient migration of COCs through the low-permeable clayey sediments of the Juana-Diaz Formation into the underlying limestone, and off site towards human and ecological receptors, PROTECO will develop an appropriate post-closure ground-water monitoring plan based on the Study's results and conclusions. If on the other hand, the Study does not identify any specific migration pathway, PROTECO will not be required to monitor ground-water during post-closure. The Study results and conclusions will be provided to USEPA Region II in a stand-alone document.

## 1.2 SITE GEOLOGY

The Site is geologically located within the clayey, clastic rocks of the Juana-Diaz Formation which completely surround and underlie the former RCRA hazardous waste units and the active landfill. Extensive site-specific hydrogeologic investigations have been conducted over a fifteen-year period by various consultants. Geologic, hydrogeologic and water resources investigations of Tallaboa Valley, Peñuelas and Ponce areas have also been conducted by government agencies such as U.S. Geological Survey, Puerto Rico Planning Board, and the Puerto Rico Department of Natural Resources. These studies all conclude that the Juana-Diaz Formation is not an aquifer. Over 100 feet of clayey sediments of the Juana-Diaz Formation, surrounding and underlying the Site, act as a low-permeable medium in

which trapped ground water stagnates in discontinuous pockets and/or moves very slowly toward the south. This ground water is highly mineralized and connate (not exposed to infiltration of fresh water from the land surface). Because of the poor natural quality and low yield of any ground water contained in the Juana-Diaz Formation, it is not a suitable source for domestic water supply or irrigation.

USEPA Region II's main concern regarding possible migration of COCs off site is related to the existence of "Reef Limestone" (Limestone) below the clayey sediments of the Juana-Diaz Formation. This Limestone is found at depths ranging from 160 to 220 feet below ground surface (bgs) with water levels ranging from 150 to 200 feet bgs (Hart Engineers, Inc., 1988; OHM Remediation Services Corp., 1994). Volatile organic compounds or other contaminants were not detected in monitoring wells screened in the Limestone, except for deep monitoring well MW-50D (now abandoned). However, the presence of volatiles in MW-50D (1,1-dichloroethene; 1,1-dichlorethane; 1,1-trans-dichlorethene; trichloroethylene; and perchloroethylene in December 1987) "may be attributed to cross-contamination during well construction" (OHM Remediation Services Corp., 1994) and not the result of COC migration into the Limestone from the overlying Juana-Diaz Formation. As discussed previously, the purpose of this Study is to evaluate the potential for downgradient migration of COCs through the low-permeable clayey sediments of the Juana-Diaz Formation into the underlying Limestone and addresses USEPA Region II's concern for potential human and ecological receptors.

# 2.0 OBJECTIVES AND TECHNICAL APPROACH SUMMARY

The objective of the Study is to assess a possible hydraulic connection between the Juana-Diaz Formation and the underlying Limestone beneath the Site, and to assess the possible presence of basin-wide discharge points for ground water in the Limestone.

The technical approach for the Study will be as follows:

## 2.1 PHASE I

- Literature Review: Review was performed during preparation of the PROTECO's supplemental submission to USEPA Region II (submittal date October 15, 1998) entitled "Relevance of ASTM Standard D 5717-95 to Hydrogeologic Conditions at Site, Peñuelas, Puerto Rico."

- Delineation of the Study area: In general, the Study area is bounded by the Tallaboa River valley west of the Site, known outcrops of the Limestone north and south of the Site, and the eastern boundary of the Site.

- Hydrologic and hydrogeologic inventory: A systematic search for water supply wells, springs, streams, other flowing water, and ponds possibly fed by ground water from the Limestone will be performed. Up to 10 potential monitoring sites will be chosen after performing the hydrologic and hydrogeologic inventory.

- Background monitoring for dyes or dye-like substances: The monitoring will be performed by installing dye detectors such as activated charcoal at each of the potential 10 monitoring sites to be monitored for dye.

## 2.2 PHASE II

- Dye injection at two locations (monitoring wells) at the Site.

- Dye monitoring (sampling) at appropriate locations (consisting of possible water supply wells, streams, springs, and monitoring well) on and off-site. The number and locations of sites to be monitored will be submitted to the USEPA Region II for approval.

- Laboratory analyses.

- Data evaluation and reporting.

The sampling and analysis procedures for this Study are described in Sections 3.6 and 4.0.

# 3.0 SCOPE OF WORK

The Scope of Work to conduct this Study is described below. Briefly, the Study includes two phases. Phase one consists of a literature review, delineation of Study area, hydrologic and hydrogeologic survey and background monitoring for dyes. Phase two consists of the injection of separate dyes in two monitoring wells located on-site, dye monitoring at the approved locations, laboratory analysis, and data evaluation and reporting.

## 3.1 PHASE ONE

### 3.1.1 Background Fluorescence Investigation

Background monitoring for dyes or dye-like substances will be performed by installing dye detectors (activated charcoal) at each of the potential monitoring sites to be monitored for dye. The locations will include selected water supply wells, streams, springs and monitoring well. Background dye concentrations will be sampled for three consecutive one-week periods. Ground water and surface water elevations will also be recorded during the monitoring period. If dyes are detected during the background monitoring, alternate dyes and/or locations may be proposed.

Ground-water elevations in monitoring wells will be determined from water level measurements and surveyed reference points. The ground-water elevations in water supply wells, and surface water elevations at springs and streams will be estimated using available topographic maps for the area.

### 3.1.2 Dye Monitoring Sites

As applicable, four types of monitoring sites may be used: water supply wells, springs, streams, and monitoring wells. The monitoring wells are located on the Site. The remaining dye monitoring sites are discussed below.

Dye monitoring sites may be identified along the sides and in the Tallaboa River valley, and along the Tallaboa River channel located generally west of the PROTECO Site. These sites will be reviewed (walked), pending suitable access arrangements, to confirm the hydrologic and hydrogeologic inventory performed during Phase I. This inventory will be performed prior to background dye monitoring as

discussed in Section 3.1. Any inflowing streams/springs will be backtracked, if possible, to the point of origin. Additional dye monitoring sites identified will be numbered, located on a map and monitored.

As a check for missed surface streams/springs and potential subsurface springs, a downgradient location in the Tallaboa River channel will be located and established as a dye monitoring Site.

Dye detectors set in springs or streams will be suspended on one of the following devices that are designed to keep them in flowing water and free of clay that may settle from suspension:

1. "Gumdrop", a hydrodynamically stable stand, will be placed into a body of water in an upright position (the gumdrop will be tested, via a string pull, to insure it is upright)
2. Rock weight with styrofoam underwater floater that suspends the dye detector above the stream bed.
3. Rock with dye detector firmly attached will be used in shallow water to insure that the dye detector remains under water in a position so that as much water as possible will flow past it.

Gumdrops and rocks are secured to a high point to facilitate recovery of the detectors if water levels rise in response to rainfall.

No data are known to be available for springs in the study area. No continuous flow data are available on the response of the Tallaboa River tributary streams to heavy rains. Based on the available data, eastern tributaries of the Tallaboa River in the study area are intermittent streams. A range of storm-response types is expected to occur.

Dye monitoring will be performed in one existing monitoring well at the Site (MW-51D) to assess the possibility of contaminant migration from the Juana-Diaz Formation into the underlying Limestone. A dye detector in this well will be set midway in the screened interval. The detector will be hung on monofilament line to which a fiberglass screen bag of marbles has been attached for weight.

## 3.2 PHASE TWO

### 3.2.1 Dye Injection Sites

There are no known sinking streams, open sinkholes, or open joints/fractures on the Site; therefore, the dye injection will be performed at the following two existing monitoring wells:

- Deep Limestone well MW-51D.

- A shallow monitoring well, close to MW-51D and completed in the clayey sediments of the Juana-Diaz Formation. This shallow monitoring well will undergo a well integrity/accessibility survey prior to finalizing well selection.

These two monitoring wells will be injected with two different types of dye as explained in Section 3.2.2.

The hydraulic gradient in the Limestone underlying the Site is both toward south (down dip) and west-northwest (along strike) (weekly data September 1986 through February 1987; OHM Remediation Services Corp., 1994). Injection of dye directly into the Limestone through monitoring well MW-51D, and monitoring for possible dye occurrences at locations described in Section 3.2, will provide information on the potential for exposure of human and ecological receptors to ground water from the Limestone. Based on the literature review, there are no known discharge points (e.g., water wells or springs) in the Limestone off Site. As explained earlier, a hydrologic and hydrogeologic inventory in the study area will be performed to assess potential discharge locations for ground water from the Limestone. The Limestone unit dips in the southerly direction under younger clayey sediments of the Juana-Diaz Formation and is several thousand feet below land surface along the sea coast.

Injection of dye into a shallow monitoring well completed in the Juana-Diaz Formation and monitoring for possible dye occurrence in the deep Limestone well MW-51D, as well as at other locations described in Section 3.2, will provide information on the potential for migration of COCs through the Juana-Diaz Formation and into the underlying Limestone.

### 3.2.2 Dyes To Be Used

The dyes planned for use are standard dyes conventionally employed for tracing ground water. Subject to evaluation and interpretation of background data, the following two fluorescent dyes will be used during the Study in the following sequence:

- First Injection: 10 lbs. of Rhodamine WT (Acid Red 388) at monitoring well MW-51D.

- Second Injection (approximately 2 days after the first one): 10 lbs. of Fluorescein (Acid Yellow 73) at the shallow monitoring well.

The dyes selected, the quantities to be used, the shallow well selected for dye injection, and the order of injection are subject to change depending on the capacity of the proposed injection well, and the background fluorescent investigation.

### 3.2.3 Dye Injection

Prior to dye injection, PROTECO will notify the Commonwealth of Puerto Rico's Department of Environment and Natural Resources, Ponce Region. Dyes will be injected at each of the two monitoring well locations by using the following three sequential steps:

1. Inject about 200 gallons of potable "primer" water into the monitoring well.
2. Inject concentrated dye solution into the hole.
3. Inject about 2,000 gallons of potable "chaser" water into the monitoring well.

Control background dye tests will be performed on the potable water used for dye injection.

If a monitoring well used for dye injection does not drain rapidly, it may be necessary to add additional potable water to facilitate draining.

### 3.2.4 Sampling Procedure For Dye Detection

Dye will be recovered on activated charcoal detectors placed in a small packet constructed from fiberglass screening (Appendix A). Activated charcoal is used to detect the fluorescent dyes, which will accumulate (sorb) on the charcoal.

Detector packets will be transported and stored in watertight and light-tight labeled plastic, zip-loc bags. Each sample will be identified by a unique sample-site identification number, site name, sampling date, and sampler initials.

Assuming that the day of initial dye injection is designated as Day 0, and if the second dye is then injected on Day 2, the following sampling schedule will be used:

**For water supply wells, spring and stream sites:** Days 0, 7, and then approximately every two weeks thereafter until the Study is deemed to be complete, but no longer than 6 months after the dye injection.

**For monitoring well MW-51D:** Days 0, 3, 7, 14, and approximately every two weeks thereafter until the Study is deemed to be complete, but no longer than 6 months after the dye injection.

The sampling intervals, as well as the sampling locations may be altered slightly to accommodate field conditions and results. Possible alterations to the anticipated schedule will be performed in coordination with USEPA, Region II.

### 3.2.5 Reporting of Results

A report describing the Study procedures and results will be submitted to the USEPA, Region II and will include the following as minimums:

- Map showing sites monitored for dye and generalized flow routes from each injection point to each dye-monitoring point, if applicable.
- Table showing dye identification and concentration at each site where dye was recovered.
- Interpretation of Study results relative to future ground-water migration and monitoring.

## 4.0 METHODS FOR DYE ANALYSES

As the dye detector packets in water supply wells, streams, and springs are collected they will be rinsed at the sampling site using stream and spring (well) water to partially remove carbon dust and accumulated mud. If the Site water is not available, the rinsing will be performed with potable water. Dye detection packets from monitoring wells should not require rinsing. The dye detector will then be sent via overnight delivery to the analytical laboratory for analysis. Final packet rinsing using potable water will be done at the laboratory.

Analysis for each of the fluorescent dyes will be performed by elution of dye from the activated charcoal in each detector. The charcoal detectors will be placed in a fan dryer and air-dried for 24 hours. One gram of charcoal will be placed into a disposable plastic container and then eluted for 60 minutes with 10 ml of an eluent consisting of 1-propanol, de-ionized distilled water and ammonium hydroxide mixed at a ratio of 5:3:2 (Smart solution). A 3.0 mL sample will then be withdrawn using a disposable polyethylene pipette and placed into a disposable rectangular polystyrene curette. Synchronous scanning on a Shimadzu spectrofluorophotometer model RF 5301 PC, or comparable equipment will then analyze the sample (Appendix B). This will yield a quantitative analysis, often with a detection limit of less than 10 parts per trillion. The remaining charcoal will be archived until the final report has been submitted and approved by USEPA Region II.

If the spectrofluorophotometer scan indicates positive results for fluorescent dye, spectrum integration will be used to determine the concentration of the dye in question. If the emission spectra from two dyes overlap, the spectra for dye will be separated by use of a non-linear curve-fitting computer program specifically designed for spectral separation. Spectrum integration will then be used to determine the concentration of each individual dye present in the sample. QA/QC protocols for dye analysis are described in Appendix B. Disposable plastic ware will be used throughout the entire analytical procedure.

Project-specific dye-standards, mixed from the same lot of dyes injected during the Study, will be prepared and used for analytical calibration.

The decision as to whether there is a positive recovery of dye is based on the following interrelated factors:

- Dye concentration at least five times the highest background.
- At least two positives (see Appendix B) at a particular dye detector location.

## 5.0 SCHEDULE

The phase one field effort will begin within two weeks after receiving approval of the Dye Tracer Study Work Plan by USEPA Region II. Background dye detectors will be placed at the locations identified during phase one. After the last set of background detectors have been collected, analyzed, and evaluated, final dye monitoring locations will be selected. The final dye monitoring locations selected will be submitted to the USEPA Region II for approval. Phase one activities are anticipated to take approximately four weeks.

Phase two activities will begin within two weeks after receiving approval of dye monitoring locations. For the purposes of estimating a schedule, USEPA Region II has been allotted two weeks to review and approve the selected dye monitoring locations. Phase two will be completed at the end of six months from date of dye injection.

A report on Study results will be submitted to USEPA Region II within 60 days after the last dye detectors have been collected in the field and analyzed.

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- *A. Response to Regulatory Questions on Part B Application*
- *B. A Draft of Special Permit Conditions*
- *C. Part B Application Revision No. 4*
- *D. Technical Specifications for the Proposed*
- *E. Response Action Outline*
- *F. Sketch of Unit 16 Final Grading Plan*
- *G. June 5, 1986 Letter from R.M. Walka to Dr. J.J. Fernandez*
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# APPENDIX A

# DYE RECEPTOR DEPLOYMENT AND RETRIEVAL

# 1.0 DYE RECEPTOR DEPLOYMENT AND RETRIEVAL

## 1.1 DYE RECEPTOR DEPLOYMENT

### 1.1.1 Dye Receptor Construction

The dye receptors will consist of small packets constructed of vinyl-coated fiberglass screen mesh. The mesh will form an enclosure for 10-grams of activated carbon. Dye receptors will be prepared in advance in a dye-free environment and individually packaged in sealable polyethylene bags. Each dye receptor will be pre-marked for its intended monitoring location.

### 1.1.2 Dye Receptor Placement

Dye receptors will be sealed in a cooler or other watertight and light-tight container under chain-of-custody procedures for transportation to the Site. The detectors will be inspected for signs of damage prior to deployment. Disposable latex gloves will be worn when handling the dye receptors in order to avoid transferring dyes from clothing and other items. Fresh gloves will be used for the placement of each dye receptor.

The dye receptors will be deployed in the water flow of the stream or resurgence point to be monitored. The dye receptors will be secured using a system of weights, floats, and tethers as necessary to secure the dye receptor in a location where flow past the dye receptor is maximized and exposure to sunlight is minimized. In areas accessible to the public, it may be necessary to make the dye receptor anchoring system inconspicuous in order to avoid tampering.

In small springs or streams, the channel may be altered by moving rocks or by other minor means in order to maximize flow past the dye receptor. In shallow water, the dye receptors may be shielded to minimize photochemical decay of dyes in the sunlight. Dye receptors will be secured so that they can be retrieved under high water conditions.

Two dye receptors will be deployed at separate nearby locations at key resurgence and stream points and at locations accessible to the public. This provides a backup in the event that the primary dye receptor is

lost or stolen. Duplicates from 10 percent of the dye receptor locations will be analyzed to evaluate quality control.

### 1.1.3 Dye Receptor Retrieval and Transport

When retrieving the dye receptor, the condition of the stream or resurgence point will be carefully examined for the presence of dye or evidence of tampering or other disturbance. The dye receptor will be retrieved from the stream/spring by means of its tether. Where wading is necessary, the dye receptor will be approached from downstream and rubber boots will be thoroughly decontaminated prior to reuse. Disposable latex gloves will be worn during handling of each dye receptor. The dye receptor will be rinsed in the water from which it was removed to clean it of accumulated sediment. The dye receptor will be placed in its original, labeled, sealable, polyethylene bag and placed in a closed container to shield it from sunlight. The dye receptor bag will be marked in permanent ink with the following data:

- Project name
- Dye receptor identification number (derivative of the inventory number)
- Name of monitored point
- Date and time of retrieval
- Initials of staff collecting the dye receptor

Dye absorbed onto charcoal dye receptors is extremely stable at ambient temperatures. Retrieved dye receptors will be transported under chain-of-custody procedures at ambient temperatures in a dark, sealed container, such as a sample cooler. If holding time of the dye receptors is more than 24 hours, they will be refrigerated to prevent mold growth.

# APPENDIX B

# LABORATORY PROCEDURES
# AND
# QUALITY ASSURANCE/QUALITY CONTROL PLAN

# 1.0 LABORATORY PROCEDURES AND QUALITY ASSURANCE/QUALITY CONTROL PLAN

## 1.1 SAMPLE CUSTODY

Dye receptors will be shipped to an analytical laboratory via overnight courier. Chain-of-custody forms are signed and the sample site name, date and time are recorded in a bound laboratory log book. One copy of the chain-of-custody form is added to the laboratory custody records and a second copy is taped to the sample container and it is locked in a refrigerator.

## 1.2 SAMPLE STORAGE

Samples are kept in a locked refrigerator in a locked laboratory to which no one but laboratory personnel have access.

## 1.3 DOCUMENTATION

Each dye receptor is kept in its original, labeled, sealed, polyethylene, zip-lock bag until it is removed from the refrigerator. The bags are opened one at a time and the receptor removed. It is washed in a high-speed jet of tap water to remove mud, a typed laboratory identification number and the original Site location number are stapled to it and it is then placed in a dryer.

## 1.4 INSTRUMENTATION

After the elution of the activated charcoal receptors, the elutant is analyzed for dye on a Shimadzu Model RF 5301PC scanning spectrofluorophotometer or comparable instrument.

## 1.5 CHARCOAL TESTING

### 1.5.1 Preparation

1. Charcoal dye receptors are washed under a high-speed jet of tap water to remove as much mud as possible.
2. A typed site location name, number and date of collection are stapled to each receptor.
3. The receptors are placed in a fan dryer and air-dried for 24 hours.
4. One gram of charcoal is weighed and placed into a disposable plastic container that is labeled with the site location number.
5. The remainder of the charcoal is returned to its original zip-lock bag and stored dark until the dye trace investigation is complete.
6. 10 ml of Smart solution (an eluent consisting of 1-propanol, de-ionized distilled water and ammonium hydroxide mixed at a ratio of 5:3:1) is added to the charcoal and the plastic container is capped.
7. After 60 minutes, a 3.0-ml sample of the elutant is withdrawn from the plastic container using a disposable polyethylene pipette and placed into a disposable rectangular polystyrene cuvette.
8. The cuvette, with the elutant equilibrated to the ambient laboratory temperature, is placed in the Shimadzu RF 5301PC spectrofluorophotometer (or comparable instrument) for analysis by synchronous scanning.

### 1.5.2 Analysis

There are no USEPA or ASTM standard methods for the analysis of fluorescent dyes. However, scientists with the most experience in performing dye tracing in aquifers are in agreement that analysis on a scanning spectrofluorophotometer provides the lowest detection limits and most reliable dye analysis. For a typical analysis for Fluorescein, Rhodamine WT, Eosine and/or Sulphorhodamine B in elutant by synchronous scanning, a Stoke Shift of 15 nanometers (nm) is used. The excitation scan is from 385 to 610 nm and the emission scan is from 400 to 625 nm. The scan speed is usually set on very fast and the sensitivity is usually set on high. The excitation bandwidth for synchronous scans is usually set at 5.0 nm and the emission bandwidth us usually set at 3.0 nm. The emission fluorescence from the synchronous scan is displayed on the monitor and plotted on a laser printer. The printout has the sample identifier, job name, date collected and scanning parameters at the bottom of the page. If the scan indicates positive results for fluorescent dye, a second printout is made utilizing spectrum integration to determine the concentration of the dye in question. If the emission spectra from two or more dyes

overlaps, then the spectra for each dye is separated by use of a non-linear curve-fitting computer program specifically designed for spectral separation. Spectrum integration is then used to determine the concentration of each individual dye present in the sample. For samples with concentrations above the level where high sensitivity scans are functional, said samples will be scanned under low sensitivity parameters. For samples whose concentration is approaching the quenching threshold, serial dilutions will be made until they can be scanned under low sensitivity parameters.

## 1.6 DYE QUANTIFICATION

### 1.6.1 Standards

Standards are prepared from the most recent dye batch supplied to the analytical laboratory by the suppliers. Standards for eluted charcoal sample analysis are prepared in the eluent to be used for eluting the dye from the charcoal. This is usually the Smart solution since applicable research indicates that it elutes more dye from the charcoal than other eluents tested. The dye concentration in the dye sample used for standard preparation is based upon the activity figure provided by the dye manufacturer. Rhodamine WT has an activity of 20 percent therefore its actual measurable concentration is 20 percent of its calculated concentration. Fluorescein usually has an activity of around 78 percent, but each varies with lot and manufacturer.

### 1.6.2 Notes on Dye Quantification

Dye concentrations are expressed in ppb. The quantity of dye absorbed by the charcoal is a function of the dye concentration in the water and the quantity, velocity, temperature and duration of exposure. Turbidity and the quantity and species of molecules competing with the dye for the charcoal acceptor sites can reduce the quantity of dye absorbed onto the charcoal. Also, the quantity of dye eluted from the charcoal is dependent on the amount of charcoal and eluent used, the type of eluent, whether the charcoal is wet or dry before elution, and the length of time the charcoal is eluted before being analyzed. The laboratory procedures can be standardized but the exposure variabilities while the receptor was in the stream cannot be. Although dye concentrations for eluted samples are measured and recorded in ppb (or often just intensity), these values will virtually always be much higher than the dye concentrations ever reached in the stream. Also, because of several water exposure variables, the concentration of dye absorbed by the charcoal does not accurately represent the quantity of dye that flowed in the stream past the dye receptor. Analysis of dye receptors placed in the same general area of the same stream for the

same time period will often result in large differences when expressed in ppb. Therefore, the following abbreviations are used to express the dye concentration in more general terms rather than ppb.

| | |
|---|---|
| - | Negative |
| + | Positive |
| ++ | Very Positive |
| +++ | Extremely Positive |
| B | Background |
| 0 | Dye receptor not recovered |

Although dye concentration cannot be accurately quantified from charcoal dye receptors, detection of dye at concentration above background fluorescence does constitute a positive trace.

## 1.7 CRITERIA FOR INTERPRETING RESULTS OF SYNCHRONOUS SCANNING

### 1.7.1 Background Dye Receptors

In order for background fluorescence to be recorded, it must meet the following conditions:

1. The recorded peak of the curve must be within + or – 5 nm for Fluorescein and Rhodamine WT.
2. The determined concentration for each dye must be 3 times the detection limit.

### 1.7.2 Regular Dye Receptors

**Negative Results** – Sample results which have a fluorescence intensity less than three times the concentration of the highest background dye receptor analyzed shall be reported as Negative

**Background Results** – Sample results which have a concentration greater than or equal to three times, but less than five times the concentration of the highest background dye receptor analyzed shall be reported as Background (B).

**Positive Results** - Sample results that is determined to be positive must meet the following criteria:

1. For sample locations which display a background concentration fluctuation more than three times the concentration of the highest background dye receptor analyzed, that sample must have a concentration 10 times the concentration of the highest background dye receptor analyzed before being reported as Positive (+).
2. For sample locations which display a background concentration fluctuation less than three times the concentration of the highest background dye receptor analyzed, that sample must have a concentration five times the fluorescence intensity of the highest background dye receptor analyzed before being reported as Positive (+).
3. The concentration of the dye eluted from the charcoal must display a rise and fall, similar to a dye breakthrough curve, over a period of time. Consequently, no location shall be called positive if three is only one occasion when the dye concentration met the above criteria. A minimum of two positives are needed in order to consider that a particular location had a positive trace.
4. The shape of the curve from the synchronous scanning must be the characteristic symmetrical shape of each particular dye as determined from its laboratory standard.

## 1.8 QUALITY CONTROL SAMPLES

### 1.8.1 Field Duplicates

Duplicate dye receptors are placed at 20 percent or more of the locations to be monitored. The second receptor serves as a back-up in the event that the primary receptor is lost or stolen. The secondary receptors are analyzed as duplicates for at least 10 percent of the total dye receptor locations.

### 1.8.2 Trip Blanks

At least two trip blanks are prepared in the laboratory and sent along with the new dye receptors to the field. The trip blanks are then kept with the old dye receptors as they are being collected in the field, returned to the laboratory, and analyzed.

### 1.8.3 Laboratory Blanks

**Eluent Blank** - Each batch of eluent solution is analyzed for each dye before it is used to elute charcoal samples.

**Charcoal Blank -** A sample from each new sealed jar of activated charcoal is eluted and analyzed for each dye before the remainder of the charcoal in the can is used.

**De-ionized Distilled Water Blank -** A de-ionized distilled water sample is analyzed to demonstrate that the dye signal on the chart produced by the spectrofluorophotometer is not generated by the instrument. One such blank is analyzed before and after each set of samples. One is also analyzed after every 20 samples.

**Laboratory Control Standards**

A low concentration standard, at the detection limit for each dye to be analyzed is analyzed before and after each set of samples. This demonstrates that the Shimadzu is capable of detection at the minimum detection limit. One is also analyzed after every 20 samples.

## 1.9 ANALYSIS ORDER

Analysis will be performed in the general sequence of no or little to high dye concentrations as follows:

1. De-ionized distilled water blank
2. Eluent blank
3. Charcoal blank
4. Laboratory control standard for each dye
5. Trip blank
6. Samples of presumed low concentration
7. Samples of presumed high concentration
8. De-ionized distilled water blank
9. Laboratory control standard for each dye